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(54) **High-strength austenitic heat-resisting steel having improved weldability**

(57) A high-strength austenitic heat-resisting steel, having improved weldability, consisting of less than 0.05 wt% C, not more than 5 wt% Si, less than 2 wt% Mn, not more than 0.03 wt% P, not more than 0.005 wt% S, 15 to 20 wt% Cr, 6 to 15 wt% Ni, 1.5 to 10 wt% W, more than 0.1 up to 0.5 wt% Nb, 0.05 to 1.5 wt% V, more than 0.15 up to 0.4 wt% N, and the balance consisting of Fe and unavoidable impurities.

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## Description

The present invention relates to an austenitic heat-resisting steel having an excellent high-temperature strength, an improved weldability, and a high resistance to grain boundary corrosion and advantageously applicable to boilers used under severe service conditions.

In planned thermal electric power generation plants, ultra-supercritical boilers will be used to achieve improved profitability and to comply with recent regulations regarding carbon dioxide gas exhaust. The conventional heat-resisting austenitic steels such as JIS SUS347H have too poor a creep rupture strength to be used under such severe conditions. New heat-resisting austenitic steels utilizing a precipitation strengthening by carbonitrides of Nb, Ti, etc. or a solid solution strengthening by Mo, etc. have been developed, as described in "Tetsu-to-Hagane (Iron and Steel)", vol. 70, page S1409 or "Thermal and Nuclear Electric Power Generation", vol. 38, page 75.

However, these new heat-resisting steels contain large amounts of alloying elements and are not more weldable than JIS SUS310S which has relatively poor weldability for a conventional austenitic heat-resisting steel, and therefore, the welding workability must be improved.

It is well known that purification of steels, including reduction in the P and S contents, and also reduction in the C content, is one of the most effective measures to improve weldability. However, many heat-resisting steels are strengthened by carbonitrides as mentioned above, and reduction in the C content would also reduce the high-temperature strength of the steels.

An object of the present invention is to provide an austenitic heat-resisting steel having a good weldability and high-temperature strength.

Regarding the steel compositions in which the C content is reduced to improve weldability, various experiments were conducted to compensate for a reduction in the high-temperature strength due to the reduced C content by adding other alloying elements, and it was finally found that a combined addition of W, Nb, V and N in an specified range will provide a synergistic effect to ensure high-strength at elevated temperatures. The steel also has a resistance to high-temperature corrosion comparable with those of conventional steels.

According to the present invention, there is provided a high-strength austenitic heat-resisting steel, having improved weldability, consisting of:

- C: less than 0.05 wt%,
- Si: not more than 5 wt%,
- Mn: less than 2 wt%,
- P: not more than 0.03 wt%,
- S: not more than 0.005 wt%,
- Cr: 15 to 20 wt%,
- Ni: 6 to 15 wt%,
- W: 1.5 to 10 wt%,
- Nb: more than 0.1 up to 0.5 wt%,
- V: 0.05 to 1.5 wt%,
- N: more than 0.15 up to 0.4 wt%, and
- the balance consisting of Fe and unavoidable impurities.

According to the present invention, there is also provided a high-strength austenitic heat-resisting steel, having improved weldability, consisting of:

- C: less than 0.05 wt%,
- Si: not more than 5 wt%,
- Mn: less than 2 wt%,
- P: not more than 0.03 wt%,
- S: not more than 0.005 wt%,
- Cr: 15 to 20 wt%,
- Ni: 6 to 15 wt%,
- W: 1.5 to 10 wt%,
- Mo: not more than 2.0 wt% and within the range defined by  $Mo + W \leq 10$  wt%,
- Nb: more than 0.1 up to 0.5 wt%,
- V: 0.05 to 1.5 wt%,
- N: more than 0.15 up to 0.4 wt%, and
- the balance consisting of Fe and unavoidable impurities.

The amounts of the alloying elements are limited as specified above for the following reasons. For simplicity, "%" is

means "wt%" in the following discussion.

C: The C amount must be reduced to as little as possible to prevent high-temperature cracking during welding or reduction in elongation. To ensure good weldability, the upper limit of the C content was determined based on the following experimental results.

Figure 1 shows a Varestraint test result indicating the weldability for steels (plots "♦") containing main components in amounts falling within the specified range of the present invention (Cr: 18%, Ni: 13%, W: 4%) except that the C content was varied, and a reference steel of JIS SUS310STB (plots "□", corresponding to Comparative Steel Q in Examples to follow). It can be seen from Fig. 1 that the weldability is better than that of JIS SUS310STB when the C content is less than 0.05%. The upper limit of the C content was thus determined to be less than 0.05%.

Si: Si is not only effective as a deoxidizer but also improves the oxidation resistance and the resistance to high-temperature corrosion. However, Si, when present in an excessive amount, reduces the creep rupture strength, the toughness and the weldability, and therefore, the Si content is limited to not more than 5%.

Mn: Mn is a deoxidizer and improves the weldability and the hot workability. However, Mn, when present in an excessive amount, causes degradation of the oxidation resistance, and therefore, the Mn content is limited to less than 2%.

Cr: Cr is essential for the oxidation resistance, resistance to steam oxidation, and resistance to high-temperature corrosion. To ensure properties comparable with or better than those of the conventional austenitic stainless steels, Cr must be present in an amount of not less than 15%. However, Cr, when present in an excessive amount, causes an increase in the Ni amount necessary to stabilize austenite and is not economical, and therefore, the Cr content is limited to not more than 20%.

Ni: Ni is essential for improving the stability of austenite and suppressing the formation of the  $\delta$  phase. In the steel according to the present invention, Ni must be present in an amount of 6% or more to stabilize austenite with respect to Cr and other ferrite formers present in the specified amounts. On the other hand, the use of Ni in a large amount is not economical, and therefore, the Ni content is limited to not more than 15%.

Mo, W: Mo and W improve the high-temperature strength by solid solution strengthening or precipitation of the Laves phase and the effect is generally described as a function of the (Mo + W)% as shown in Fig. 2. It can be seen from Fig. 2 that, when the total amount of Mo and W is 2% or more, the creep rupture strength is sharply improved and the improvement is not substantially increased if the total amount of Mo and W is more than 10%.

When the W amount or the total amount of Mo and W is 1.5 to 2.0%, the creep rupture strength substantially varies with the amounts of C and Nb. When the amounts of C and Nb are 0.025% or more and 0.25% or more, respectively, an improved creep rupture strength is obtained through a synergistic or combined effect of the W or W + Mo amount and the C + Nb amount. However, the synergistic effect is not obtained when the W or W + Mo amount is less than 1.5%.

Mo and W, when present in a total amount of more than 10%, also cause a problem in that the Laves phase and other intermetallic compounds coarsen and reduce the creep rupture strength.

Moreover, when Mo is added alone or not combined with W, the resistance to high-temperature corrosion is reduced with increase of the Mo amount as shown in Fig. 3. On the other hand, W, even when added alone or not combined with Mo, does not cause reduction in the resistance to high-temperature corrosion, and when combined with Mo, improves the resistance to high-temperature corrosion in comparison with that achieved when Mo alone is added. Therefore, W must be present in an amount of 1.5 to 10%. Mo may be present in combination with W but the Mo content must not be more than 2.0% because the resistance to high-temperature corrosion is sharply reduced when the Mo content is more than 2.0%, even when combined with W.

Nb: Nb sharply improves the long duration creep rupture strength by the formation of fine carbonitrides. To achieve this effect, the Nb content must be 0.1% or more as can be seen from Fig. 4. The effect becomes more significant as the Nb amount is increased within a range in which Nb is completely dissolvable in a solid solution state. However, when the Nb amount is more than this range, undissolved carbides and nitrides are retained to reduce the creep rupture strength. Therefore, the Nb amount must not be more than 0.5%.

V: V forms fine nitrides and improves the long duration creep rupture strength. As shown in Fig. 5, this effect is obtained when the V amount is 0.05% or more and the improvement is reduced when the V amount is more than 1.5%. Therefore, the V amount is 0.05 to 1.5%.

P: P forms phosphides and improves the long duration creep rupture strength as shown in Fig. 6. However, P, when present in an excessive amount, sharply reduces not only the weldability but also the hot workability, and therefore, the P must not be present in an amount of more than 0.03%.

S: S segregates at crystal grain boundaries and reduces the hot workability and also facilitates the grain boundary embrittlement under the creep condition, and therefore, the S content is limited to not more than 0.005%.

N: N sharply improves the creep rupture strength by solid solution strengthening and the formation of nitrides. To compensate for the strength reduction because of the reduced C content for ensuring an improved weldability, N must be present in an amount of more than 0.15%. However, when N is present in an amount of more than 0.4%, the improvement in the long time creep rupture strength is not substantially increased but the toughness is reduced. There-

fore, the N content is more than 0.15% and up to 0.4%.

Figure 1 is a graph showing a Vareststraint test result for steels containing elements other than C in amounts within the specified range of the present invention, in comparison with the result for a JIS SUS310STB steel;

Fig. 2 is a graph showing the creep rupture strength as a function of the W + Mo content;

Fig. 3 is a graph showing the resistance to high-temperature corrosion as a function of the amounts of W and Mo;

Fig. 4 is a graph showing the creep rupture strength as a function of the Nb content;

Fig. 5 is a graph showing the creep rupture strength as a function of the V content; and

Fig. 6 is a graph showing the creep rupture strength as a function of the P content.

The present invention will be described in detail by way of the following examples.

#### EXAMPLES

Tables 1-1 and 2-1 summarize the chemical compositions and the properties of the steels tested. After being subjected to a solid solution heat treatment at 1250°C, the steels were subjected to a Vareststraint test, a creep rupture test at 700, 750 and 800°C, and a high-temperature corrosion test at 650°C. The Vareststraint test was carried out using the GTAW welding method, under the conditions of a test piece thickness of 4 mm, a welding voltage of 10V, a welding current of 80A, a welding speed of 80 mm/min, and an applied strain of 4%. The creep rupture data were standardized by the Larson-Miller method to estimate the creep rupture strength at 650°C for 100,000 hours. The high-temperature corrosion strength was carried out in a simulated combustion ash having the composition of  $K_2SO_4:Na_2SO_4:Fe_2(SO_4)_3 = 0.28:0.2:0.5$  (by weight), in which the steels were held at 650°C for 200 hours and the corrosion weight loss was determined. The test results are summarized in Tables 1-2 and 2-2.

The steels A to Q in Tables 1-1 and 1-2 are the present inventive steels and the steels R to AI in Tables 2-1 and 2-2 are comparative steels. In the comparative steels, Steels R and S correspond to JIS SUS347H and JIS SUS310S, respectively, which are commonly used in the conventional art. The present inventive steels A to Q have a remarkably improved high-temperature strength and resistance to high-temperature corrosion in comparison with the comparative steel R or JIS SUS347H and an improved weldability in comparison with the comparative steel S or JIS SUS310S. The comparative steels S to V have a poor weldability and exhibit a large total crack length in the Vareststraint test. The comparative steels X to Z contain W in amounts less than the present inventive range and the comparative steels AE, AF, AG contain Nb, V and N in amounts less than the present inventive ranges, respectively, so that all these comparative steels X to AG have a poor high-temperature strength. The comparative steels AA to AD contain Mo in an amount more than the present inventive range and have an improved high-temperature strength but have a poor resistance to high-temperature corrosion.

The inventive steel P and the comparative steels W and AH demonstrate the synergistic effect of the combined addition of W with C and Nb, in which the inventive steel P contains more than 0.025% C and more than 0.25% Nb and has an improved high-temperature strength even though the W content is near the lower limit of the specified range, whereas the comparative steel W contains less than 0.025% C and less than 0.25% Nb and has a poor high-temperature strength and the comparative steel AH contains W in an amount less than the lower limit of the specified range and has a poor high-temperature strength although C and Nb are present in amounts more than 0.025% and 0.25%, respectively.

The comparative steel AI contains an excessive amount of P and has an improved high-temperature strength but has a poor weldability.

As herein described above, the present invention provides a high-strength austenitic heat-resisting steel, having an improved weldability, which is inexpensive and commercially applicable.

Table 1-1

|           |   | Chemical Composition (wt%) |      |      |       |       |      |      |      |      |      |      |      |
|-----------|---|----------------------------|------|------|-------|-------|------|------|------|------|------|------|------|
|           |   | C                          | Si   | Mn   | P     | S     | Cr   | Ni   | W    | Mo   | Nb   | N    | V    |
| Invention | A | 0.015                      | 0.20 | 1.03 | 0.010 | 0.004 | 17.6 | 12.8 | 3.95 | -    | 0.20 | 0.19 | 0.10 |
|           | B | 0.026                      | 0.21 | 1.03 | 0.011 | 0.003 | 17.5 | 12.8 | 3.75 | -    | 0.20 | 0.19 | 0.10 |
|           | C | 0.041                      | 0.20 | 1.02 | 0.011 | 0.004 | 17.6 | 12.9 | 4.06 | -    | 0.21 | 0.19 | 0.11 |
|           | D | 0.018                      | 0.49 | 0.94 | 0.010 | 0.002 | 17.2 | 7.3  | 2.43 | -    | 0.21 | 0.21 | 0.09 |
|           | E | 0.014                      | 0.49 | 0.94 | 0.009 | 0.002 | 18.2 | 12.3 | 2.91 | -    | 0.21 | 0.19 | 0.09 |
|           | F | 0.017                      | 0.50 | 1.43 | 0.013 | 0.004 | 16.6 | 12.2 | 6.25 | -    | 0.21 | 0.18 | 0.11 |
|           | G | 0.018                      | 0.48 | 0.96 | 0.012 | 0.005 | 17.4 | 13.5 | 8.08 | -    | 0.20 | 0.19 | 0.10 |
|           | H | 0.015                      | 0.21 | 0.97 | 0.007 | 0.002 | 17.9 | 11.5 | 2.86 | 1.53 | 0.20 | 0.18 | 0.11 |
|           | I | 0.016                      | 0.20 | 0.96 | 0.011 | 0.004 | 17.5 | 12.5 | 3.95 | -    | 0.42 | 0.19 | 0.11 |
|           | J | 0.015                      | 0.20 | 0.92 | 0.010 | 0.004 | 17.5 | 12.3 | 4.02 | -    | 0.21 | 0.20 | 0.29 |
|           | K | 0.015                      | 0.20 | 0.91 | 0.009 | 0.004 | 17.5 | 12.3 | 4.03 | -    | 0.21 | 0.20 | 0.59 |
|           | L | 0.014                      | 0.20 | 0.90 | 0.009 | 0.004 | 17.4 | 12.3 | 4.00 | -    | 0.21 | 0.22 | 1.48 |
|           | M | 0.018                      | 2.10 | 0.96 | 0.009 | 0.004 | 16.2 | 14.8 | 3.73 | -    | 0.21 | 0.21 | 0.12 |
|           | N | 0.016                      | 4.12 | 0.96 | 0.009 | 0.004 | 16.4 | 12.3 | 3.73 | -    | 0.21 | 0.20 | 0.11 |
|           | O | 0.016                      | 0.51 | 0.98 | 0.005 | 0.002 | 19.5 | 15.0 | 3.91 | -    | 0.21 | 0.29 | 0.10 |
|           | P | 0.027                      | 0.25 | 1.49 | 0.008 | 0.001 | 18.0 | 9.1  | 1.51 | -    | 0.26 | 0.18 | 0.30 |
|           | Q | 0.021                      | 0.39 | 1.01 | 0.028 | 0.002 | 17.8 | 8.1  | 2.49 | -    | 0.20 | 0.20 | 0.11 |

Table 1-2

|           |   | Total Crack Length in<br>Varestraint Test (mm) | Creep Rupture Strength<br>at 650°C for 10 <sup>5</sup> hours<br>(MPa) | Corrosion Weight Loss<br>at 650°C for 200 hours<br>(mg/cm) |
|-----------|---|--|---|--|
| Invention | A | 0.7  | 150   |  |
|           | B | 1.8  | 140   |  |
|           | C | 4.9  | 135   |  |
|           | D | 1.2  | 120   |  |
|           | E |  | 125   | 260  |
|           | F |  | 160   |  |
|           | G |  | 180   | 281  |
|           | H |  | 130   | 255  |
|           | I |  | 150   |  |
|           | J |  | 165   |  |
|           | K |  | 180   |  |
|           | L |  | 170   |  |
|           | M |  | 150   |  |
|           | N |  | 150   |  |
|           | O |  | 130   |  |
|           | P |  | 120   |  |
|           | Q | 3.1  | 135   |  |

Table 2-1

|    | Chemical Composition (wt%) |      |      |        |       |       |       |       |       |       |       |      |
|----|----------------------------|------|------|--------|-------|-------|-------|-------|-------|-------|-------|------|
|    | C                          | Si   | Mn   | P      | S     | Cr    | Ni    | W     | Mo    | Nb    | N     | V    |
| R  | 0.050*                     | 0.49 | 1.36 | 0.014  | 0.005 | 18.3  | 11.3  | - *   | -     | 0.98* | 0.01* | - *  |
| S  | 0.078*                     | 0.52 | 1.45 | 0.008  | 0.004 | 24.8* | 19.7* | - *   | -     | - *   | 0.02* | - *  |
| T  | 0.062*                     | 0.20 | 0.98 | 0.011  | 0.003 | 17.7  | 12.8  | 4.04  | -     | 0.20  | 0.17  | 0.11 |
| U  | 0.078*                     | 0.19 | 0.99 | 0.009  | 0.003 | 17.6  | 12.9  | 4.03  | -     | 0.20  | 0.19  | 0.09 |
| V  | 0.102*                     | 0.20 | 0.97 | 0.009  | 0.003 | 17.6  | 12.9  | 4.01  | -     | 0.21  | 0.20  | 0.09 |
| W  | 0.016                      | 0.21 | 0.97 | 0.011  | 0.002 | 17.9  | 8.1   | - *   | -     | 0.22  | 0.17  | 0.09 |
| X  | 0.014                      | 0.52 | 1.02 | 0.011  | 0.001 | 18.2  | 8.3   | 0.52* | -     | 0.21  | 0.18  | 0.09 |
| Y  | 0.015                      | 0.51 | 0.98 | 0.011  | 0.001 | 18.2  | 8.6   | 1.51* | -     | 0.21  | 0.20  | 0.11 |
| Z  | 0.014                      | 0.20 | 0.95 | 0.009  | 0.004 | 17.1  | 7.5   | - *   | 1.52  | 0.21  | 0.19  | 0.11 |
| AA | 0.014                      | 0.51 | 0.97 | 0.008  | 0.002 | 17.8  | 12.1  | - *   | 3.07* | 0.22  | 0.16  | 0.09 |
| AB | 0.017                      | 0.51 | 0.98 | 0.013  | 0.005 | 17.7  | 19.5* | - *   | 8.92* | 0.21  | 0.19  | 0.10 |
| AC | 0.014                      | 0.21 | 0.95 | 0.007  | 0.002 | 17.8  | 13.9  | 2.92  | 3.02* | 0.21  | 0.17  | 0.11 |
| AD | 0.012                      | 0.22 | 0.96 | 0.010  | 0.002 | 17.7  | 22.3* | 2.93  | 8.87* | 0.21  | 0.16  | 0.11 |
| AE | 0.016                      | 0.20 | 1.45 | 0.011  | 0.004 | 17.5  | 12.3  | 3.96  | -     | 0.05* | 0.19  | 0.10 |
| AF | 0.014                      | 0.18 | 0.95 | 0.010  | 0.004 | 17.6  | 12.5  | 4.05  | -     | 0.21  | 0.20  | - *  |
| AG | 0.012                      | 0.49 | 0.97 | 0.010  | 0.003 | 17.6  | 14.9  | 3.94  | -     | 0.21  | 0.05* | 0.09 |
| AH | 0.029                      | 0.21 | 1.47 | 0.008  | 0.001 | 18.1  | 9.0   | 1.01* | -     | 0.31  | 0.18  | 0.30 |
| AI | 0.023                      | 0.28 | 1.15 | 0.051* | 0.001 | 18.0  | 8.8   | 2.48  | -     | 0.22  | 0.19  | 0.20 |

Note: The symbol "\*" means that the value is outside the specified range.

Table 2-2

|            |    | Total Crack Length in<br>Varestraint Test (mm) | Creep Rupture Strength<br>at 650°C for 10 <sup>5</sup> hours<br>(MPa) | Corrosion Weight Loss<br>at 650°C for 200 hours<br>(mg/cm) |
|------------|----|--|---|--|
| Comparison | R  |  | 70  |  |
|            | S  | 5.8  | -   |  |
|            | T  | 6.5  | 135   |  |
|            | U  | 7.6  | 145   |  |
|            | V  | 8.2  | 140   |  |
|            | W  |  | 100   | 249  |
|            | X  |  | 105   |  |
|            | Y  |  | 105   | 239  |
|            | Z  |  | 110   | 305  |
|            | AA |  | 130   | 376  |
|            | AB |  | 175   | 578  |
|            | AC |  | 160   | 312  |
|            | AD |  | 170   | 494  |
|            | AE |  | 105   |  |
|            | AF |  | 115   |  |
|            | AG |  | 100   |  |
|            | AH |  | 105   |  |
|            | AI | 6.3  | 150   |  |

### Claims

1. A high-strength austenitic heat-resisting steel having improved weldability, consisting of:

C: less than 0.05 wt%,  
 Si: not more than 5 wt%,  
 Mn: less than 2 wt%,  
 P: not more than 0.03 wt%,  
 S: not more than 0.005 wt%,  
 Cr: 15 to 20 wt%,  
 Ni: 6 to 15 wt%,  
 W: 1.5 to 10 wt%,  
 Nb: more than 0.1 up to 0.5 wt%,  
 V: 0.05 to 1.5 wt%,  
 N: more than 0.15 up to 0.4 wt%, and  
 the balance consisting of Fe and unavoidable impurities.

2. A high-strength austenitic heat-resisting steel having improved weldability, consisting of:

C: less than 0.05 wt%,  
 Si: not more than 5 wt%,  
 Mn: less than 2 wt%,  
 P: not more than 0.03 wt%,



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S: not more than 0.005 wt%,

Cr: 15 to 20 wt%,

Ni: 6 to 15 wt%,

W: 1.5 to 10 wt%,

Mo: not more than 2.0 wt% and within the range defined by  $Mo + W \leq 10$  wt%,

Nb: more than 0.1 up to 0.5 wt%,

V: 0.05 to 1.5 wt%,

N: more than 0.15 up to 0.4 wt%, and

the balance consisting of Fe and unavoidable impurities.

Fig.1

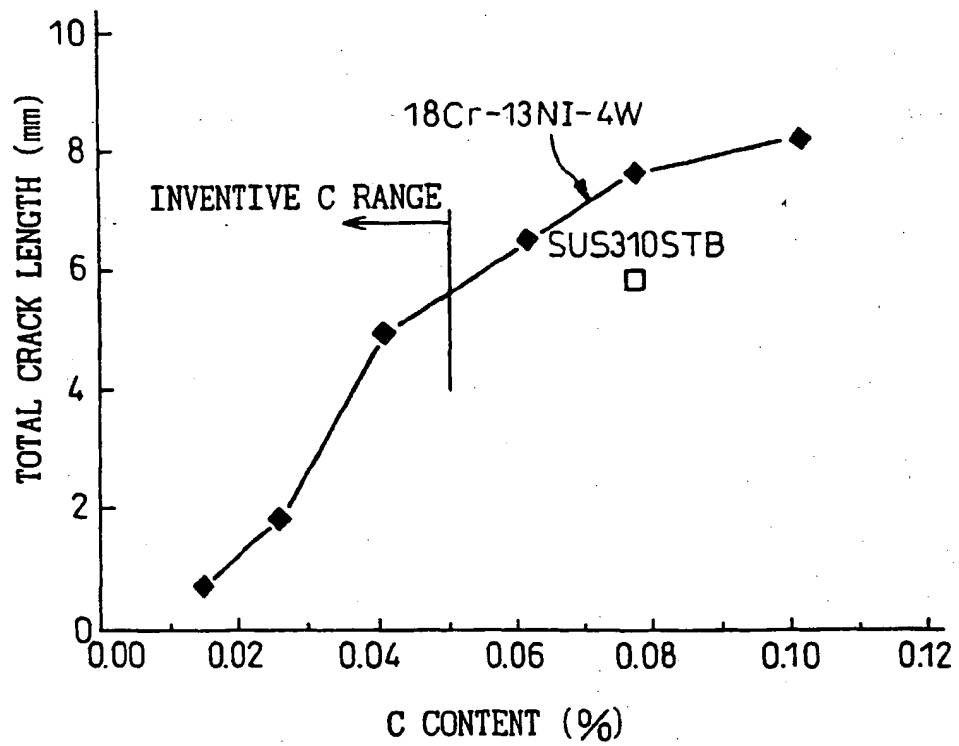


Fig. 2

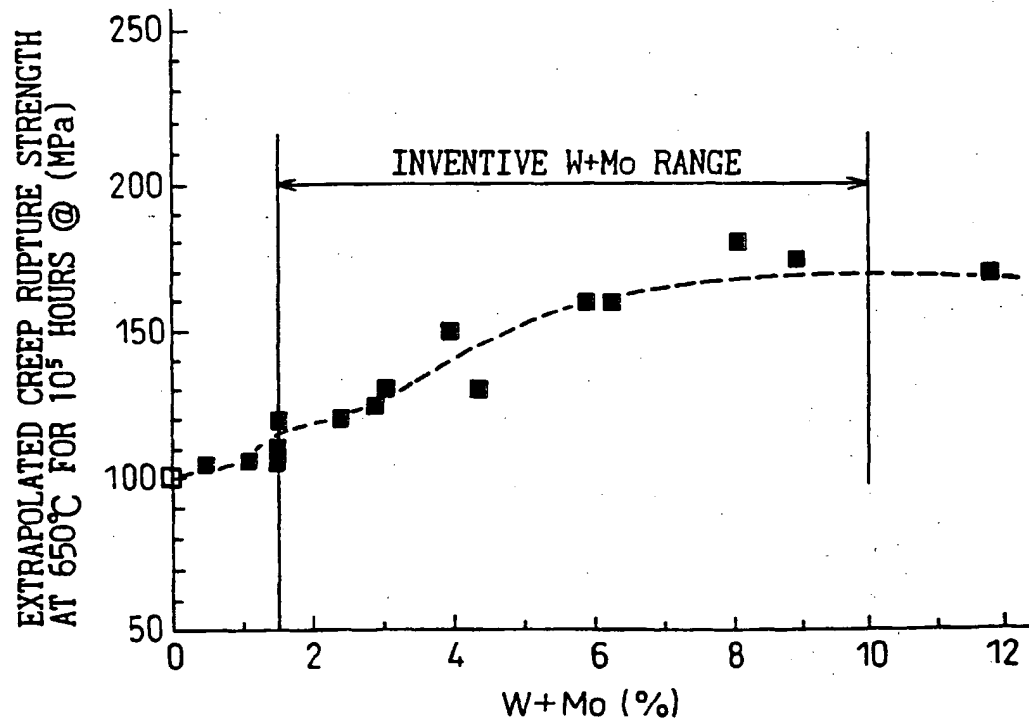


Fig. 3

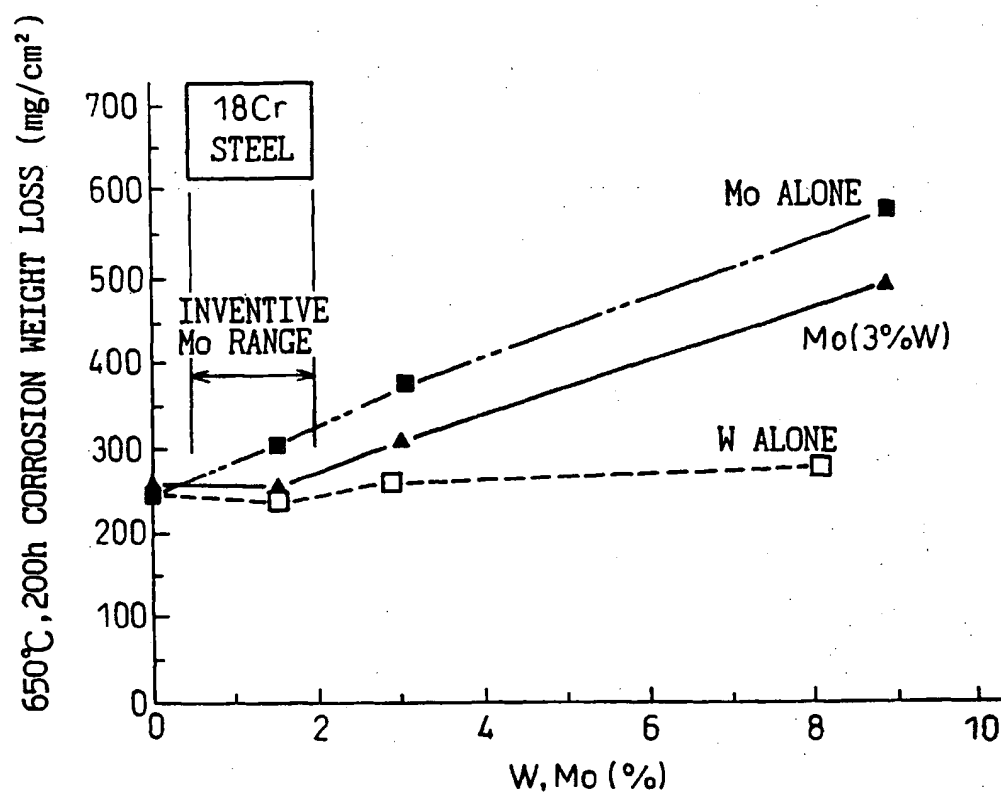


Fig. 4

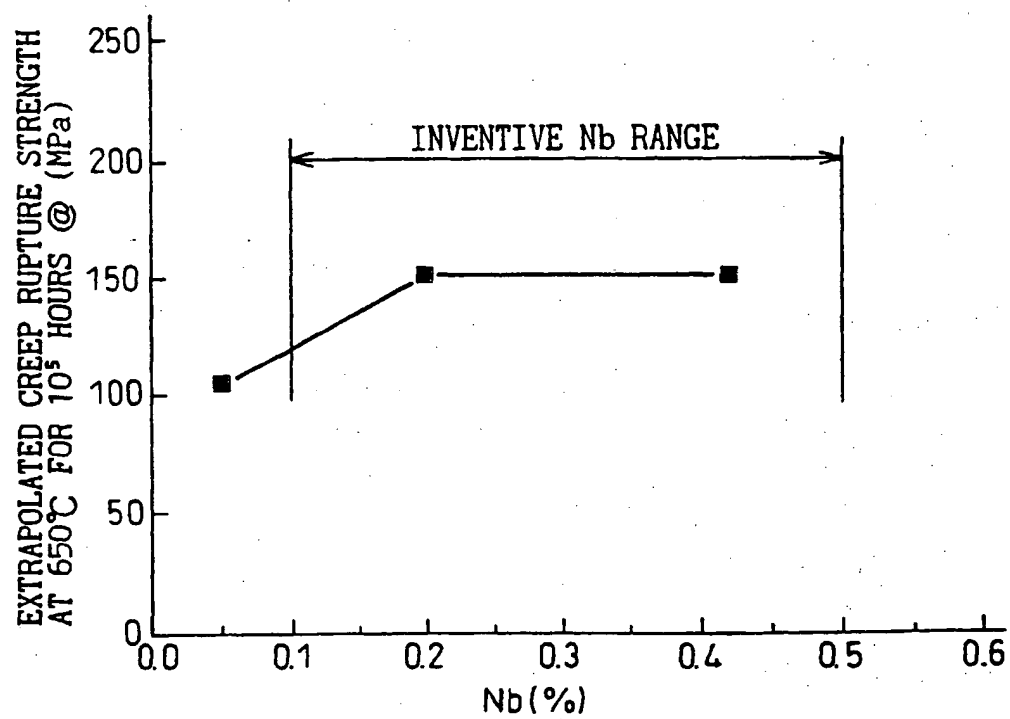


Fig.5

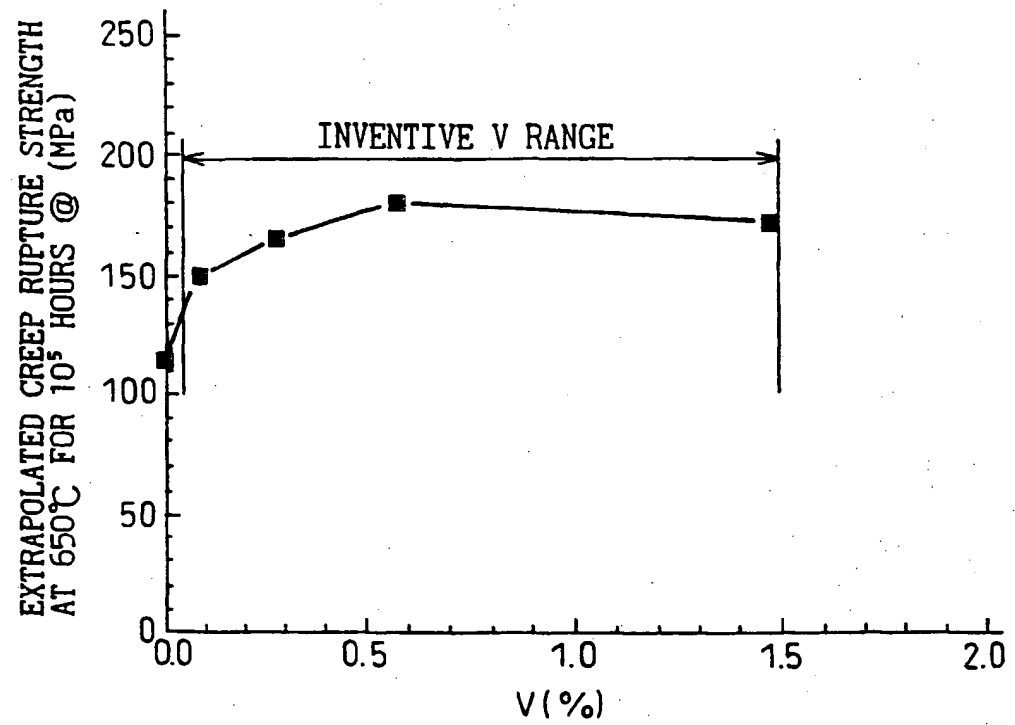
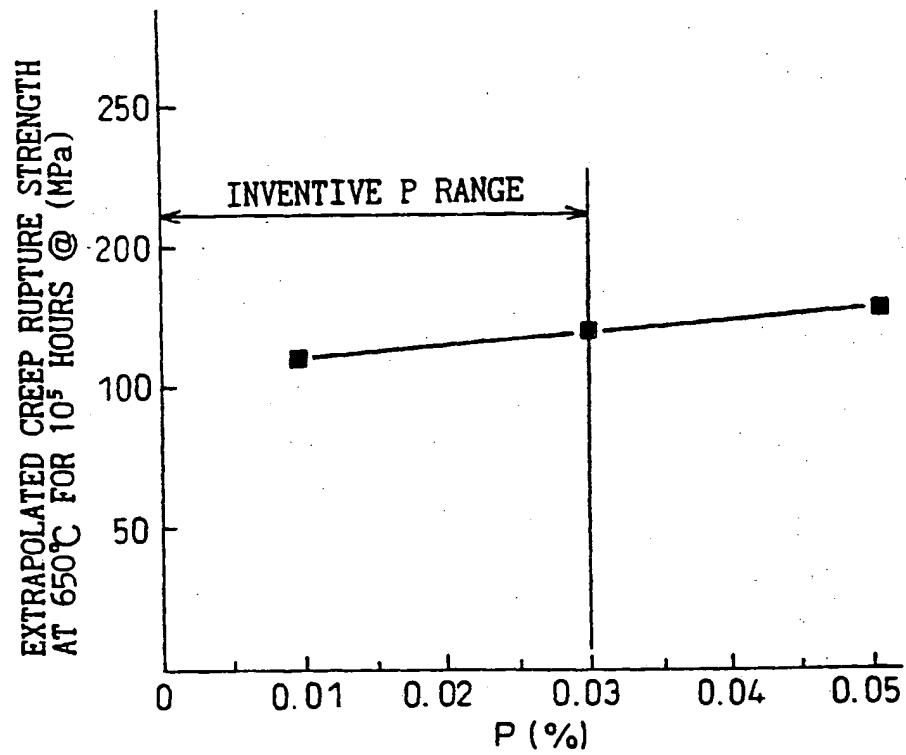


Fig. 6





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 96 12 0536

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |   |  |
|---|--|---|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim                                 | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| A   | EP 0 178 374 A (TOKYO SHIBAURA ELECTRIC CO) 23 April 1986<br>* Claims 1 and 10; page 5, lines 12-14; page 6, lines 29-33 * | 1,2   | C22C38/44<br>C22C38/46<br>C22C38/48          |
| A   | GB 1 224 898 A (UGINE KUHLMANN) 10 March 1971<br>* Claim 1; Table 1 *  | 1,2   |  |
| A   | GB 617 194 A (HAYNE STELLITE COMPANY) 2 February 1949<br>* Claim 1,2; page 2, lines 64-69; page 3, lines 10-35 *           | 1,2   |  |
| A   | US 3 693 245 A (CADENET JEAN-JACQUES DE) 26 September 1972   | 1,2   |  |
|   |  |   | TECHNICAL FIELDS SEARCHED (Int.Cl.6)         |
|   |  |   | C22C   |
| The present search report has been drawn up for all claims  |  |   |  |
| Place of search<br>MUNICH   |  | Date of completion of the search<br>27 March 1997 | Examiner<br>Bjoerk, P                        |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p> |  |   |  |

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